Fluorescence Studies of Nd^{+3} Ions in Phosphate Glass

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Abstract: Tripositive neodymium ion doped phosphate glass has been prepared by melt-quenching technique. The final composition (by weight) was approximately $Na(PO_3)_6$70%-BaO15%-PbO 10%-Al_2O_3 5%-R Ln (Where R=0.5% and Ln= Nd^{+3}). The experimental oscillator strengths were calculated from the areas under the absorption bands. Judd-Offelt parameters (Ω_λ) evaluated using the observed spectral intensities have been used to compute various laser parameters *viz.*, spontaneous emission probability (A), radiative life time (τ) and stimulated emission cross-section (σ_p). The bonding environment surrounding the rare earth (RE) ion has also been discussed.

Keywords: Phosphate glass, Fluorescence spectrum, Absorption spectrum, Radiative properties

Introduction

Phosphate Glasses are both scientifically and technologically important materials because they generally offer some unique physical properties better than other Glasses[1]. Phosphate glass exhibit very important physical properties such as low melting temperature, high thermal expansion coefficient, low glass transition temperature, low softening temperature and high UV transmission[2,3]. Despite their solubility, the low processing temperature has led these glasses to be used in applications such as glass to metal seals, low temperature enamels for metals and for optical elements[4].

Also the optical properties like transparency at the excitation and the lasing wavelengths, the spectroscopic properties of the lasing ion, thermo-optic properties, nonlinear optical properties, the fundamental absorption edge and absorption by multiphonon processes depend upon the composition of inorganic glass forming systems and modifiers[5,6]. The choice of suitable glass formers and modifiers help in tailoring the laser glass to meet the specific requirements. One of the first solid-state lasers was demonstrated in 1961 in Nd^{+3} doped glasses. Lasing in an Nd^{+3} doped multi component glass fiber was reported three years later. The same material structure was exploited to demonstrate the first thin-film waveguide glass amplifier, in 1972[7] and the first integrated optical glass laser, in 1974[8]. Since then, many remarkable results in the development of more efficient glass matrices and in the actual fabrication of rare-earth-doped glass integrated optical amplifiers have been achieved[9-11].

Recently, we have carried out fluorescence of Nd^{3+} doped phosphate glass with a view to develop suitable glass for laser action in the visible region. Judd-Offelt parameters (Ω_λ) evaluated using the observed spectral intensities have been used to compute various laser parameters *viz.*, spontaneous emission probability (A), radiative life time (τ) and stimulated emission cross-section (σ_p) for different fluorescence lines have been evaluated.

Experimental

Rare earth doped Phosphate glass was prepared by melt quenching technique. The composition (by weight) was approximately $Na(PO_3)_6$70%-BaO15%-PbO 10%-Al_2O_3 5%-R Ln (Where R=0.5% and Ln= Nd^{+3}) from reagents of analytical grade in 10 g batches. The Nd_2O_3 ion added to the host glass matrix was 99.99% purity. The glass material was mixed in an agate pestle mortar for two hours and was thermally treated for 4 hours in a platinum crucible at 1200 ± 25 ^{0}C. Homogeneity of the melt was ensured by stirring the melt with a platinum rod from time to time. The melt was quenched by pouring into rectangular shaped mould placed on a steel plate. The glass specimen was polished using cerium oxide powder and again annealed. The glass specimens contained no crystalline phase as revealed by x-ray diffractogram of the specimen.

The fluorescence spectrum was recorded using a Perkin Elmer Luminescence spectrophotometer model LS50B in the spectral range 200-900 nm. The absorption spectrum was recorded at room temperature in the visible region using a double beam spectrophotometer with a resolution of 0.5 nm. The length and width of the rectangular glass specimen was measured with the help of Vernier calliper, while the path length was measured with a screw gauge. The refractive index of glass specimens were measured on an Abbé refractometer (ATAGO 3T). An ordinary lamp was used as the light source.

Results and Discussion

Eight bands have been observed in the absorption spectrum and they have been assigned by comparing their positions with the energy level scheme of LaF_3: Nd^{3+}, published by Carnall *et. al.*[12] All transitions in the absorption spectrum of Nd^{3+} start from the ground state $^4I_{9/2}$ to the various excited states, their peak position and assignments have been given in Table 2.

Table 1. Fluorescence transition and radiative properties of phosphate glass with 0.5 wt % doping concentration of Nd^{3+} ion

Transitions	$\lambda_{max,}$ nm	A, sec^{-1}	τ, μsec	σ_p, 10^{-20}, cm^2
$^4F_{3/2}\rightarrow {}^4I_{9/2}$	882	1391.926	718	1.408

Table 2. Experimental oscillator strength (P_{exp}) measured (S_{exp}) calculated (S_{cal}) absorption line strengths and Judd- ofelt intensity parameters for the Nd^{3+} doped Phosphate glass:

Absorption bands	λ, nm	$P_{exp,}10^{-6}$	S_{exp}, 10^{-20}	S_{cal}, 10^{-20}	ΔS, 10^{-20}
$^4I_{9/2}\rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	798	7.74	4.179	4.054	0.124
$^4F_{7/2,} {}^4S_{3/2}$	748	6.85	3.394	3.561	-0.167
$^4F_{9/2}$	680	0.94	0.431	0.265	0.165
$^4G_{5/2,} {}^2G_{7/2}$	583	17.50	6.908	6.890	0.017
$^4G_{7/2}$	526	5.62	1.996	1.386	0.609
$^4G_{9/2}$	511	2.56	0.886	0.580	0.305
$^2P_{1/2,} {}^2D_{5/2}$	432	0.67	0.195	0.231	-0.036
$^4D_{3/2,} {}^4D_{1/2}$	350	8.90	2.107	0.186	1.920

$\Omega_2 = 3.1029, \Omega_4 = 5.9872, \Omega_6 = 4.9870$

The intensities of the observed bands have been measured in terms of line strength S_{exp}, calculated from the observed oscillator strength of the absorption bands, have also been included in Table 2. These values serve as a basis for the calculation of the three phenomenological parameters, Ω_{λ}, (λ= 2, 4, 6), known as Judd-Offelt parameters[13,14]. The Judd-Offelt intensity parameters Ω_2, Ω_4 and Ω_6 found by least squares fit method[15,16] have been presented in Table 2 for the Nd^{3+} doped Phosphate glass. The calculated line strengths (S_{cal}) have been compared with the experimental measured line strengths (S_{exp}).

In the phosphate glass specimen it has been observed that $\Omega_4 > \Omega_6 > \Omega_2$. The most intense band in the Absorption spectra of Nd^{+3} doped phosphate glass specimens around 350 nm ($^4I_{9/2} \rightarrow {}^4D_{3/2}$, $^4D_{1/2}$) has been used for the excitation wavelength. As a consequence of which one fluorescence band around 882 is observed, it has been assigned to the transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$.

In the case of Nd^{+3} doped phosphate glass specimens the values of spontaneous emission probability (A) is high for $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. Stimulated emission cross section (σ_p) is a most important laser parameter. Its value signifies the rate of energy extraction from the laser material. The value of stimulated emission cross section (σ_p) is also higher for the above transition suggesting that under suitable circumstances, it can be used as a good laser transition. The values of A, τ, σ_p have been shown in Table 1 for Nd^{+3} doped glass specimen. The value of fluorescence branching ratio (β) is calculated in those cases where more than one transition is observed.

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